5-Bromo-2-hydroxybenzaldehyde thiosemicarbazone

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The molecule of the title compound, $C_8H_8BrN_3OS$, is close to being planar, with maximum deviations of -0.127 (3) and 0.135 (5) Å for the N atoms of the –NH– and NH_2– groups, respectively. Intramolecular N—H$\cdots$N and O—H$\cdots$N hydrogen bonds to the same acceptor N atom generate $S(5)$ and $S(6)$ ring motifs. In the crystal structure, molecules are connected into [010] chains by pairs of N—H$\cdots$S hydrogen bonds with $R_2^2(8)$ graph-set motifs. The crystal used for data collection was found to be an inversion twin.

Related literature

For background on the biological activities and pharmaceutical properties of thiosemicarbazones and their derivatives, see: Casas *et al.* (2000); Ferrari *et al.* (2000); Maccioni *et al.* (2003). For bond-length data, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).
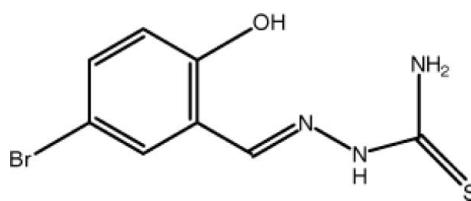
Experimental

Crystal data

$C_8H_8BrN_3OS$	$V = 1031.50$ (8) Å^3
$M_r = 274.14$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 4.4564$ (2) Å	$\mu = 4.16$ mm^{-1}
$b = 8.3515$ (3) Å	$T = 296$ K
$c = 27.7153$ (14) Å	$0.13 \times 0.09 \times 0.05$ mm

Data collection

Stoe IPDS II diffractometer	9532 measured reflections
Absorption correction: integration (X-$RED32$; Stoe & Cie, 2002)	1934 independent reflections
$T_{min} = 0.614$, $T_{max} = 0.819$	1782 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.063$	
$S = 1.04$	
1934 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
144 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
4 restraints	Absolute structure: Flack (1983), with 744 Freidel pairs
	Flack parameter: 0.477 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—HO1$\cdots$N1	0.81 (3)	1.97 (4)	2.685 (4)	149 (5)
N3—HN3$\cdots$N1	0.87 (4)	2.30 (4)	2.688 (5)	107 (3)
N2—HN1$\cdots$S1^i	0.84 (3)	2.55 (3)	3.373 (3)	168 (3)
N3—HN2$\cdots$S1^{ii}	0.86 (3)	2.50 (3)	3.363 (4)	176 (6)

Symmetry codes: (i) $-x - 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x - 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: X-$AREA$ (Stoe & Cie, 2002); cell refinement: X-$AREA$; data reduction: X-$RED32$ (Stoe & Cie, 2002); program(s) used to solve structure: $SIR97$ (Altomare *et al.*, 1999); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 2008); molecular graphics: $ORTEP$-3 (Farrugia, 1997); software used to prepare material for publication: $WinGX$ (Farrugia, 1999).

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supporting information

5-Bromo-2-hydroxybenzaldehyde thiosemicarbazone

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S1. Comment

Thiosemicarbazones constitute an important class of *N*,*S* donor ligands due to their propensity to react with a wide range of metals (Casas *et al.*, 2000). Thiosemicarbazones exhibit various biological activities and have therefore attracted considerable pharmaceutical interest (Maccioni *et al.*, 2003; Ferrari *et al.*, 2000). We here report the crystal structure of the title compound (I).

The title molecule (I) shown in Fig. 1 is almost planar with the maximum deviations of -0.127 (3) Å for N2 and 0.135 (5) Å for N3. All bond lengths and angles are normal (Allen *et al.*, 1987). In each independent molecule, there are intramolecular N—H⋯N and O—H⋯N hydrogen bonds, generating the *S*(5) and *S*(6) ring motifs, respectively (Table 1, Fig. 2).

In the crystal structure, adjacent molecules are linked by N—H⋯S hydrogen bonds, forming $R_2^2(8)$ dimers (Bernstein *et al.*, 1995) (Table 1, Fig. 2).

S2. Experimental

A mixture of 5-bromosalicylalehyde (0.01 mol) and hydrazinecarbothioamide (0.01 mol) in 20 ml of ethanol was refluxed for about 2 h. On cooling, the solid separated was filtered and recrystallized from ethanol to yield colourless prisms of (I).

S3. Refinement

The H atoms of the O—H, N—H and NH_2 groups were found from a difference Fourier map and their positional parameters were constrained [O1—H1 = 0.81 (3) and N2—HN1 = 0.84 (3), N3—HN2 = 0.86 (3) and N3—HN3 = 0.87 (4) Å]. Their isotropic displacement parameters were refined with $U_{iso}(H) = 1.2U_{eq}(N)$ for the NH and NH_2 groups and $U_{iso}(H) = 1.5U_{eq}(O)$ for hydroxyl group. The remaining H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$.
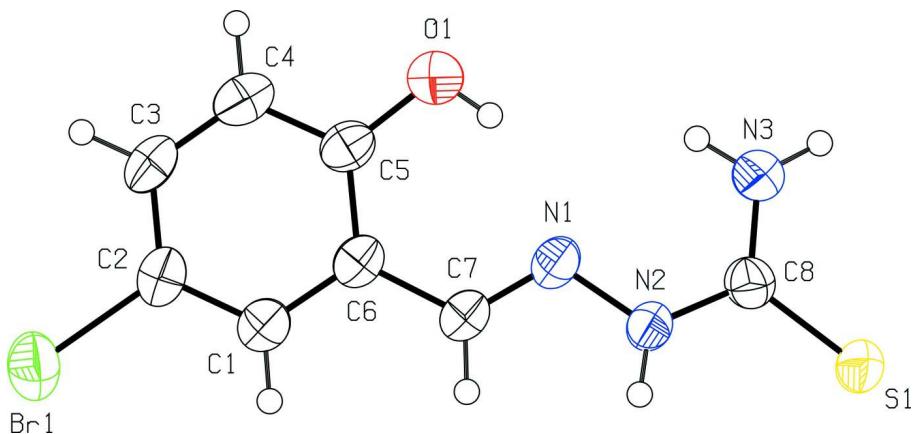
Figure 1

View of the title molecule, showing displacement ellipsoids for non-H atoms drawn at the 50% probability level.
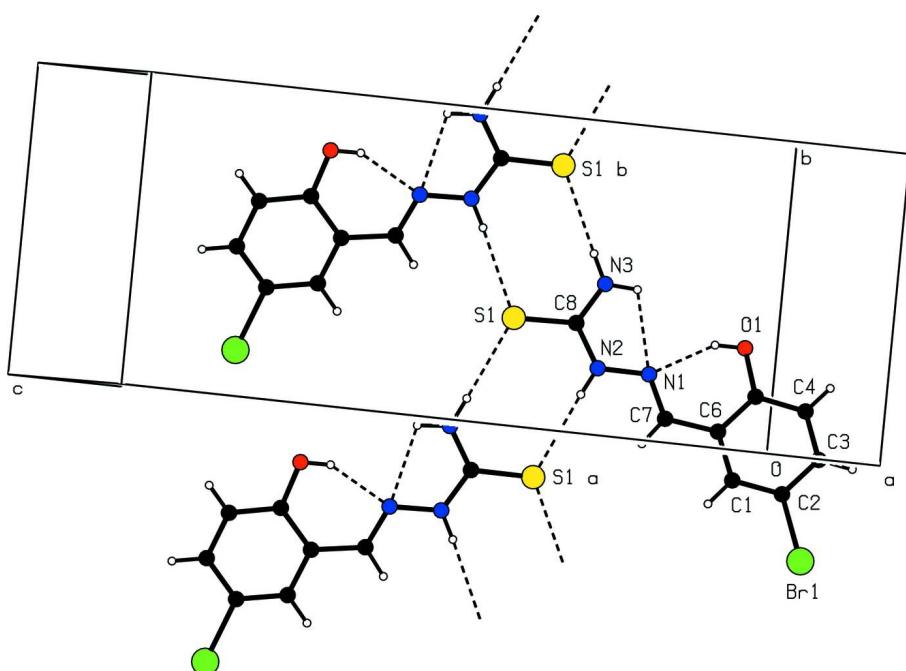
Figure 2

View of the hydrogen bonding interactions of (I), showing dimer formation by $R^2_2(8)$ ring motif within chains.

5-Bromo-2-hydroxybenzaldehyde thiosemicarbazone

Crystal data

$C_8H_8BrN_3OS$	$F(000) = 544$
$M_r = 274.14$	$D_x = 1.765$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 17874 reflections
$a = 4.4564$ (2) Å	$\theta = 1.5–26.1°$
$b = 8.3515$ (3) Å	$\mu = 4.16$ mm^{-1}
$c = 27.7153$ (14) Å	$T = 296$ K
$V = 1031.50$ (8) Å^3	Prism, colourless
$Z = 4$	$0.13 \times 0.09 \times 0.05$ mm

Data collection

Stoe IPDS II diffractometer	$T_{min} = 0.614$, $T_{max} = 0.819$
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	9532 measured reflections
	1934 independent reflections
Plane graphite monochromator	1782 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{int} = 0.037$
ω scans	$\theta_{max} = 25.6°$, $\theta_{min} = 2.6°$
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	$h = -5 \rightarrow 5$
	$k = -10 \rightarrow 10$
	$l = -33 \rightarrow 33$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.063$	
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 0.5533P]$
1934 reflections	where $P = (F_o^2 + 2F_c^2)/3$
144 parameters	$(\Delta/\sigma)_{max} < 0.001$
4 restraints	$\Delta\rho_{max} = 0.54$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.29$ e Å^{-3}
	Absolute structure: Flack (1983), with 744 Freidel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.477 (11)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.80875 (10)	−0.32853 (5)	0.06313 (1)	0.0606 (1)
S1	−0.5577 (2)	0.35791 (11)	0.26412 (3)	0.0517 (3)
O1	0.2883 (6)	0.3331 (3)	0.08454 (10)	0.0596 (9)
N1	−0.0227 (7)	0.2201 (3)	0.16022 (10)	0.0407 (9)
N2	−0.2226 (8)	0.2237 (3)	0.19824 (9)	0.0408 (9)
N3	−0.2703 (13)	0.4940 (4)	0.19194 (14)	0.0786 (16)
C1	0.4380 (8)	−0.0920 (4)	0.10693 (12)	0.0416 (10)
C2	0.6401 (7)	−0.1207 (4)	0.07038 (11)	0.0420 (10)
C3	0.7260 (8)	0.0001 (5)	0.03956 (13)	0.0486 (11)
C4	0.6033 (8)	0.1505 (5)	0.04464 (12)	0.0485 (11)
C5	0.3981 (7)	0.1819 (5)	0.08111 (11)	0.0418 (10)
C6	0.3119 (8)	0.0589 (4)	0.11293 (11)	0.0382 (9)
C7	0.0966 (8)	0.0836 (4)	0.15148 (11)	0.0389 (10)
C8	−0.3365 (8)	0.3610 (4)	0.21496 (11)	0.0416 (10)

H1	0.38530	−0.17450	0.12780	0.0500*
HN2	−0.323 (12)	0.587 (3)	0.2025 (16)	0.089 (16)*
HN1	−0.260 (9)	0.135 (3)	0.2114 (12)	0.050 (11)*
H3	0.86620	−0.01980	0.01540	0.0580*
HO1	0.169 (8)	0.334 (6)	0.1064 (12)	0.071 (14)*
H4	0.65840	0.23180	0.02350	0.0580*
HN3	−0.144 (9)	0.486 (5)	0.1681 (12)	0.071 (14)*
H7	0.04290	−0.00320	0.17060	0.0470*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0606 (2)	0.0575 (2)	0.0638 (2)	0.0057 (2)	0.0074 (2)	−0.0153 (2)
S1	0.0657 (6)	0.0400 (5)	0.0495 (5)	−0.0007 (5)	0.0199 (4)	−0.0055 (4)
O1	0.0646 (16)	0.0493 (14)	0.0649 (15)	0.007 (2)	0.0180 (14)	0.0102 (14)
N1	0.0400 (16)	0.0458 (16)	0.0364 (13)	−0.0052 (13)	0.0067 (12)	−0.0039 (11)
N2	0.0436 (18)	0.0372 (14)	0.0415 (14)	−0.0028 (13)	0.0117 (13)	−0.0030 (11)
N3	0.122 (4)	0.0397 (17)	0.074 (2)	0.011 (2)	0.051 (3)	0.0063 (17)
C1	0.0408 (17)	0.0454 (19)	0.0387 (17)	−0.0065 (16)	0.0004 (15)	−0.0037 (15)
C2	0.0341 (18)	0.0532 (19)	0.0386 (16)	−0.0029 (14)	0.0002 (13)	−0.0098 (14)
C3	0.038 (2)	0.065 (2)	0.0428 (17)	−0.0032 (18)	0.0111 (15)	0.0010 (16)
C4	0.0427 (19)	0.062 (2)	0.0407 (16)	−0.0058 (19)	0.0012 (13)	0.0095 (17)
C5	0.0368 (17)	0.0475 (19)	0.0411 (15)	−0.0069 (17)	0.0005 (12)	0.0020 (15)
C6	0.0320 (14)	0.0477 (18)	0.0350 (15)	−0.0045 (17)	−0.0008 (15)	−0.0019 (13)
C7	0.0374 (19)	0.0462 (18)	0.0332 (15)	−0.0033 (15)	0.0027 (13)	−0.0010 (14)
C8	0.0465 (18)	0.0381 (18)	0.0402 (15)	−0.0006 (17)	0.0002 (15)	−0.0030 (13)

Geometric parameters (Å, º)

Br1—C2	1.902 (3)	C1—C2	1.377 (5)
S1—C8	1.682 (3)	C1—C6	1.390 (5)
O1—C5	1.358 (5)	C2—C3	1.376 (5)
O1—HO1	0.81 (3)	C3—C4	1.377 (6)
N1—N2	1.380 (4)	C4—C5	1.388 (5)
N1—C7	1.281 (4)	C5—C6	1.407 (5)
N2—C8	1.337 (4)	C6—C7	1.451 (5)
N3—C8	1.315 (5)	C1—H1	0.9300
N2—HN1	0.84 (3)	C3—H3	0.9300
N3—HN2	0.86 (3)	C4—H4	0.9300
N3—HN3	0.87 (4)	C7—H7	0.9300
C5—O1—HO1	107 (4)	O1—C5—C4	117.7 (3)
N2—N1—C7	115.6 (3)	C5—C6—C7	122.6 (3)
N1—N2—C8	121.9 (3)	C1—C6—C5	118.5 (3)
C8—N2—HN1	122 (2)	C1—C6—C7	119.0 (3)
N1—N2—HN1	116 (2)	N1—C7—C6	122.7 (3)
HN2—N3—HN3	120 (4)	N2—C8—N3	118.1 (3)
C8—N3—HN2	122 (3)	S1—C8—N2	119.4 (3)

C8—N3—HN3	117 (3)	S1—C8—N3	122.5 (3)
C2—C1—C6	120.7 (3)	C2—C1—H1	120.00
Br1—C2—C3	119.6 (3)	C6—C1—H1	120.00
C1—C2—C3	120.7 (3)	C2—C3—H3	120.00
Br1—C2—C1	119.7 (2)	C4—C3—H3	120.00
C2—C3—C4	119.7 (3)	C3—C4—H4	120.00
C3—C4—C5	120.6 (4)	C5—C4—H4	120.00
C4—C5—C6	119.9 (4)	N1—C7—H7	119.00
O1—C5—C6	122.5 (3)	C6—C7—H7	119.00
C7—N1—N2—C8	172.0 (3)	C2—C3—C4—C5	1.2 (5)
N2—N1—C7—C6	−179.8 (3)	C3—C4—C5—O1	179.2 (3)
N1—N2—C8—S1	−175.2 (3)	C3—C4—C5—C6	−0.6 (5)
N1—N2—C8—N3	4.9 (5)	C4—C5—C6—C1	0.4 (5)
C2—C1—C6—C7	179.1 (3)	O1—C5—C6—C1	−179.5 (3)
C2—C1—C6—C5	−0.7 (5)	O1—C5—C6—C7	0.7 (5)
C6—C1—C2—Br1	180.0 (3)	C4—C5—C6—C7	−179.4 (3)
C6—C1—C2—C3	1.2 (5)	C1—C6—C7—N1	177.9 (3)
Br1—C2—C3—C4	179.8 (3)	C5—C6—C7—N1	−2.3 (5)
C1—C2—C3—C4	−1.5 (5)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H*O*1···N1	0.81 (3)	1.97 (4)	2.685 (4)	149 (5)
N3—H*N*3···N1	0.87 (4)	2.30 (4)	2.688 (5)	107 (3)
N2—H*N*1···S1^i	0.84 (3)	2.55 (3)	3.373 (3)	168 (3)
N3—H*N*2···S1^{ii}	0.86 (3)	2.50 (3)	3.363 (4)	176 (6)

Symmetry codes: (i) −*x*−1, *y*−1/2, −*z*+1/2; (ii) −*x*−1, *y*+1/2, −*z*+1/2.